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(54) Title: IONIC LIQUIDS			
(57) Abstract			
<p>This invention relates to an ionic liquid comprising a ternary melt of (a) a compound of the formula: R_nMX_{3-n} wherein R is a C_1-C_6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1, or 2; (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide; and (c) at least one of a hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide. These ionic liquids can be used as catalysts for the oligomerization or polymerization of olefins and also for the alkylation of paraffins, isoparaffins and aromatics with olefins.</p>			

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IONIC LIQUIDS

This invention relates to novel ionic liquids and to the use thereof as the reaction medium and catalyst for various chemical reactions such as eg producing olefin polymers, especially butene polymers from raffinates I and II from a refining process and which
5 contain *inter alia* a mixture of butene-1, butene-2 and iso-butene.

Ionic liquids are primarily mixtures of salts which melt below room temperature. Such salt mixtures include aluminium halides in combination with one or more of imidazolium halides, pyridinium
10 halides or phosphonium halides and the latter being preferably substituted. Examples of the latter include one or more of 1-methyl-3-butyl imidazolium halides, 1-butyl pyridinium halide and tetrabutyl phosphonium halides.

It is known to use these ionic liquids as solvents and as catalysts for eg the dimerization and /or oligomerization of olefins
15 such as ethylene, propylene, butene-1 and/or butene-2 and for the alkylation of benzene using alkyl halides. In this context Jeffrey A Boon et al states in an article in the Journal of Organic Chemistry, Vol 51, 1986, pp 480-483 that:

"Completely ionic liquids are not the usual solvent for organic
20 reactions. Most ionic liquids are liquid only at high temperatures and offer little advantage over the more commonly used aqueous or organic media. Most work on organic reactions in molten salts have employed eutectic mixtures, but they still require temperatures above 200°C."

25 This article further goes on to state that:

"Numerous other substituted imidazolium and pyridinium chlorides form molten salts with aluminium chloride but do not possess the favourable physical properties we sought for this investigation."

5 From the above, it is clear that not all ionic liquids possess the properties desirable for specific reactions in which they are to be used and that the choice of specific ionic liquids for a given reaction is far from straightforward.

10 A further article by Yves Chauvin et al in J Chem Soc, Chem Comm, 1990, pp 1715-1716 also emphasises this point. In this article, the authors intend to carry out catalytic dimerization of alkenes by nickel complexes in organochloroaluminate molten salts to the exclusion of all other products. Moreover, the authors state that:

15 "However, it seems that no attempt has been made to take advantage of the solubility of the organometallic catalyst and the insolubility of the reaction products of the catalytic reaction in these solvents."

The authors add that:

20 "In the absence of any nickel complex, acidic melts catalyse the formation of oligomers, the molecular weight of which is characteristic of a cationic reaction".

To further add to the unpredictability of these reactions, French Patent No. 2611700 (Institut Francais du Petrole) describes a
25 process for the oligomerization of olefins including *inter alia* butene-1 and butene-2 using a nickel catalyst in the liquid phase; the catalyst used is specifically a nickel complex dissolved in an ionic liquid, the latter being the liquid phase.

30 More recently, FR-A-2626572 describes a process for alkylation using as catalyst an ionic liquid comprising at least one halide of aluminium or boron and at least one quaternary ammonium halide. The quaternary ammonium halide can be a dialkyl imidazolium halide.

35 From the above it will be clear that the function of ionic liquids in these reactions is far from predictable. Furthermore, none of the publications referred to above disclose ionic liquids

comprising alkyl substituted imidazolium halides in which any of the alkyl substituents has more than 4 carbon atoms.

It has now been found that ternary melts comprising a mixture of various quaternary ammonium halides and aluminium halides perform very well as ionic liquid catalysts.

Accordingly, the present invention is an ionic liquid which comprises a ternary melt of:

- (a) a compound of the formula R_nMX_{3-n} wherein R is a C1-C6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1 or 2,
- (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide, and
- (c) at least one of hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide.

The compound (a) in the ternary melt is suitably an aluminium halide or a gallium halide, such as aluminium trichloride or gallium trichloride, or, an alkyl aluminium/gallium halide such as an alkyl aluminium/gallium dihalide or a dialkyl aluminium/gallium halide, and is preferably ethyl aluminium/gallium dichloride.

The component (b) in the ionic liquid is at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide. These may be suitably selected from 1-alkyl-3-alkyl imidazolium halides and 1-alkyl pyridinium halides. Specific examples of these compounds include the following: 1-methyl-3-ethyl imidazolium chloride, 1-ethyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium bromide, 1-methyl-3-propyl imidazolium chloride, 1-methyl-3-hexyl imidazolium chloride, 1-methyl-3-octyl imidazolium chloride, 1-methyl-3-decyl imidazolium chloride, 1-methyl-3-dodecyl imidazolium chloride, 1-methyl-3-hexadecyl imidazolium chloride, 1-methyl-3-octadecyl imidazolium chloride, ethyl pyridinium bromide, ethyl pyridinium chloride, ethylene pyridinium dibromide, ethylene pyridinium dichloride, butyl pyridinium chloride and benzyl pyridinium bromide.

As will be appreciated, in the case of a symmetrical molecule

such as a 1,3-disubstituted imidazolium halide, it would be possible to interchange the position of the substituents in the 1- and 3-positions or to have each of the substituents in the 1- and 3-positions with 5 or more carbon atoms in the alkyl group.

5 Furthermore, it would also be possible to have the chloride ion in the compounds listed above interchanged with bromide or iodide ions to produce compounds which are equally effective as ionic liquids.

A feature of the present invention is that where the chain length of at least one of the alkyl chains in the imidazolium halide, especially the alkyl chain in the 3-position, is greater than 4
10 carbon atoms, the catalytic activity of ionic liquids comprising such halides is increased for polymerization reactions with respect to alkyl chains having 4 carbon atoms or less in that higher molecular weight products are obtained where this is desirable. The
15 performance of such ionic liquids is particularly superior when the feedstock being polymerised is a raffinate I, raffinate II or isobutene.

The component (c) in the ternary melts of the present invention is at least one of a hydrocarbyl-substituted quaternary ammonium
20 halide and a hydrocarbyl-substituted phosphonium halide. Of the substituent groups in the ammonium halides at least one substituent is an alkyl group. The other substituents may be the same or different groups selected from hydrogen, alkyl, aryl, aralkyl and alkaryl groups. Similarly, the hydrocarbyl substituted phosphonium
25 halides contain at least one hydrocarbyl group. The other substituents may be the same or different groups selected from hydrogen, alkyl, aryl, aralkyl and alkaryl groups. Specific examples of such compounds include *inter alia* the tetra alkyl ammonium or phosphonium halides, especially those in which the alkyl group has 1-
30 18 carbon atoms.

The ternary melts of the present invention are suitably prepared by mixing the components in an atmosphere inert under the reaction conditions as described in our published EP-A-0558187. It is preferable to purify each of the components in the melt prior to
35 preparing the melt. Thus, aluminium trichloride can be purified by

repeated sublimations until the melt at the bottom of the sublimator is clear and the aluminium trichloride takes on a lustrous, shiny appearance; the hydrocarbyl substituted imidazolium or pyridinium halides can be purified by repeated recrystallisations from solutions thereof in a suitable solvent; and the hydrocarbyl substituted quaternary ammonium or phosphonium halide can be purified by dissolving the halide in a suitable solvent such as eg ethanol and precipitation of the halide from the ethanol solution by dilution with eg diethyl ether followed by filtration and drying in an inert atmosphere.

Ionic liquids comprising the ternary melts of the present invention can be used in any of the reactions in which ionic liquids in general are capable of acting as a catalytic component. Thus for instance, the ionic liquids of the present invention can be used eg for alkylation and polymerisation reactions.

Where these ionic liquids are used as catalysts for the alkylation reaction, this may be either the alkylation of isoparaffins such as isobutane with a C2-C4 olefin such as eg ethylene, to produce alkylates which enhance the octane rating of fuels, or, for the alkylation of aromatics with an olefins such as eg the conversion of benzene to ethyl benzene with a view to producing styrene therefrom. The alkylation reaction is suitably carried out at a temperature of eg below 100°C, suitably from -30 to +50°C. The ratio of the catalytic ionic liquid phase to the hydrocarbon phase used for alkylation would largely depend upon the reactivity of the olefin and the acidity of the particular ionic liquids chosen. As a general guide the mole ratio of catalyst to olefins is suitably in the range from 1000 : 1 to 1 : 1000. In terms of the volume ratio of catalyst phase to hydrocarbon phase, this would suitably be in the range from in the range from 100 : 1 to 1 : 100, and more preferably from 20 : 1 to 1 : 20.

Where an iso-paraffin is being alkylated with an olefin, the ratio of iso-paraffins to olefin is suitably in the range from 1000 : 1 to 1 : 1000

Thus, according to a further embodiment, the present invention

is a process for the polymerization of an olefinic feedstock comprising one or more of C2-C4 olefins, said process comprising bringing the feedstock into contact with an ionic liquid comprising a ternary melt of:

- 5 (a) a compound of the formula R_nMX_{3-n} wherein R is a C1-C6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1 or 2,
- (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide, and
- 10 (c) at least one of a hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide
- such that the melting point of the ionic liquid is below the reaction temperature.

The components (a), (b) and (c) can be the same and have the
15 same characteristics as those described above in respect of the ternary melts of the present invention described above.

The polymerization products referred to herein are meant to include:

- i. oligomers which are conventionally defined as "a very low
20 molecular weight polymer in which the number of repeating units equals 2-10" (see Polymer Chemistry, An Introduction by R B Seymour and C E Carraher, 2nd Edition, 1988, p 14, and published by Marcel Dekker Inc), and
- ii. polymers which have at least 11 repeating units, ie an average
25 molecular weight of 600 to 100,000.

The hydrocarbon feedstock for this process is suitably ethylene, propylene, butene-1, butene-2 and/or isobutene but is preferably a raffinate from the refining process and can be raffinate I or raffinate II.

30 Raffinate I is usually the butadiene raffinate which is a by-product formed during the thermal or catalytic cracking (whether or not fluid) operation in a refinery and principally comprises C4 hydrocarbons especially a mixture of butene-1, butene-2 and iso-butene along with some saturated hydrocarbons. More specifically,
35 such raffinate I comprises at least 10% w/w of iso-butene, from 20-

40% w/w of butene-1 and butene-2, and from 10-20% w/w of butanes.

Raffinate II is the unpolymerised by-products recoverable when Raffinate I is subjected to polymerization using eg Lewis acid catalysts or the by-product gases resulting from the production of the lead-free anti-knock compound, methyl tertiary butyl ether (MTBE). In both processes the by-products have substantially the same composition and are rich in n-butenes. These by-products are the so called "raffinate II" and typically contain from 30-55% w/w of butene-1, about 10% w/w of cis-butene-2, about 17% w/w of trans-butene-2, upto 6% w/w of iso-butene and upto 30% w/w of the saturated C4 hydrocarbons n-butane and iso-butane. Since raffinate II, an otherwise wasted material, is capable of being cationically polymerized to polybutenes, its value as raw material is readily apparent.

The relative ratios of the two components (a), (b) and (c) in the ionic liquid should be such that they are capable of remaining in the liquid state under the reaction conditions. Typically, the relative mole ratio of compound (a) to the components [(b) + (c)] in the ionic liquid is suitably in the range from 1 : 2 to 3.0 : 1, preferably from 1.5 : 1 to 2 : 1. Within this range, where the ionic liquid is intended for use as a reaction medium or a solvent, the amount of the component (a) can be less than 50 mole % of the total ionic liquid. However, where the ionic liquid is intended for use as a catalyst, the amount of component (a) is preferably greater than 50 mole % of the total ionic liquid. The relative mole ratios of (b) : (c) is suitably in the range from 0.01 : 1 bearing in mind that within this range the ratios chosen should be such that the resultant ionic liquid should be a liquid at room temperature.

The polymerization reaction is suitably carried out at a temperature from -50°C to +100°C, preferably from -30°C to +70°C. The reaction can be carried out either:

- (i) by bubbling the olefinic hydrocarbon feedstock to be polymerized through the ionic liquid, or,
- (ii) by dispersing the ionic liquid in appropriate concentration into the olefinic hydrocarbon feedstock to be polymerized and

then subjecting such a dispersion to polymerization.

In the case of (i), the rate at which the olefinic hydrocarbon feedstock is to be bubbled and in the case of (ii), the amount of ionic liquid mixed with the feedstock and, in both cases the reaction temperature used will depend upon the molecular weight of the product desired. Normally in this type of reaction one would expect that the higher the temperature used, the lower the molecular weight of the polymer formed.

Irrespective of the nature of the reaction in which such ionic liquids are used as catalysts, eg oligomerization, polymerisation, alkylation or isomerisation, the reaction pressures used should be such that the components of the ionic liquid remain in the liquid phase during the reaction.

It has now been found that, surprisingly, when any of the processes, especially oligomerization, polymerisation or alkylation is used, the reaction product forms a separate phase from the ionic liquid. This product phase is substantially free of any catalyst or ionic liquid contaminants. The product can thus be readily separated from the ionic liquid eg by tapping. This feature has several advantages:

A. Ease of separation of the product polymer from the catalytic component means that further undesirable reactions eg of the olefinic end-group in the polymer, such as eg isomerization, is minimised thereby retaining the structure of the polymer formed. This also means that such further undesirable reactions are avoided without resort to the use of conventional reaction quenching agents such as aqueous alkali.

B. The product formed need not be water-washed because of the relatively low levels of the catalytic ionic liquid in the product thereby avoiding a process step.

C. The ease of separation of the product from the ionic liquid catalyst means that the catalyst can be recycled and thereby reduces operational costs.

If process (ii) is used, it may be necessary to add a quenchant such as aqueous ammonia in order to terminate the reaction and/or to

neutralise any catalytic components. The products can then be water-washed and the product polymer separated. In this case, the unreacted material can be allowed to evaporate and the dried product isolated.

5 A further feature of the present invention is that this method enables a much higher percentage of n-butenes to be incorporated in the product polymer than would be possible in conventional cationic polymerization processes using eg aluminium trichloride or boron trifluoride.

10 Yet another surprising feature of the present process is that, contrary to expectations, the molecular weight of the polymer product does not increase with decreasing temperatures. In spite of using reaction temperatures which are substantially higher than those used in the prior art, the present process gives rise to polymers which
15 have a higher molecular weight than the oligomers formed by said prior art processes.

These surprising features give a very desirable outlet for relatively low value feedstocks such as raffinates I and II at the same time making maximum use of the reactive carbon values in that
20 feedstock and hence reducing the wastage of any hydrocarbon values in such feedstock.

The polymer products produced by the process of the present invention can be used eg as lubricants or cutting fluids in the industry without further treatment. Alternatively, these polymers
25 can be maleinised and converted to corresponding succinic anhydride derivatives which in turn can be converted into the corresponding imide which is a detergent for lube oils and fuels.

The present invention is further illustrated with reference to the following Examples. In Tables below, the intensity referred to
30 is the peak height which corresponds to the number of protons in that position. In this respect the notations very strong, strong, medium and weak represent the following range of peak intensities (I/I₀):

very strong	-	80-100
strong	-	60-80
35 medium	-	40-60

weak	-	20-40
very weak	-	<20
δ (ppm)	-	chemical shift in parts per million

5 EXAMPLE 1:

A. Purification of aluminium trichloride:

In an inert-atmosphere box, anhydrous aluminium trichloride (ca. 200 g) was placed in a sublimator with sodium chloride (2 g) and powdered aluminium (1 g). The apparatus was transferred to a vacuum
10 line where the mixture was heated in vacuo in a silicone oil-bath, to 150°C. The aluminium trichloride was left to sublime until ca. 10% of it remained at the bottom of the sublimator together with the molten NaCl and impurities. After cooling, the apparatus was placed back into the inert-atmosphere box where the sublimed AlCl_3 was
15 removed by scraping and then placed again into a clean apparatus with NaCl (2 g) for re-sublimation. (Powdered aluminium was utilized in the first sublimation only, to remove iron impurities). Five successive sublimations were carried out until the melt observed at the bottom of the sublimator was clear and the AlCl_3 took on a
20 lustrous, shiny appearance.

B. Preparation of 1-ethyl-3-methylimidazolium chloride:

The preparation was carried out in a fume cupboard. The apparatus comprised a round-bottomed flask provided with an additional funnel and was adapted to be heated to elevated
25 temperature. The apparatus was purged clean with nitrogen and the reaction was carried out under nitrogen. 1-Methylimidazole (300 ml), which had previously been distilled in vacuo over KOH, was placed in the flask under nitrogen. Acetonitrile (ca. 150 ml, distilled over CaH_2) was then added to the flask. The mixture was then heated
30 slowly in small increments until the internal temperature of the flask was 68°C and then allowed to stabilize for one day. The nitrogen purge was then replaced with a stream of ethyl chloride which was administered through a flow meter at the rate of 2 dm³ ethyl chloride per hour for two days. Thereafter, the flow of ethyl
35 chloride was reduced to 1 dm³ per hour and maintained at this rate

for a further three days. After this duration, a solution containing the desired product was removed from the flask whilst still hot by cannula and this solution was extracted with ethyl acetate and small white crystals of 1-ethyl-3-methylimidazolium chloride were recovered from the extract. Further purification was carried out by recrystallisation from aliquots of ethyl ethanoate.

C. Purification of tetra-ethylammonium chloride:

Tetra-ethylammonium chloride (100 g) was dissolved in ethanol (150 ml). Diethyl ether was then added to this solution until tetra-ethylammonium chloride started to precipitate. The solution was cooled to -13°C and left at this temperature overnight. The resulting crystals were filtered under dry nitrogen and then heated in a Schlenk round bottomed flask to 100°C under vacuum for 48 hours. The resulting solid was then transferred to a dry box ready to use.

D. Preparation of Ternary melt:

Crystalline 1-ethyl-3-methylimidazolium chloride was melted in vacuo and poured into an aluminium foil "boat" under an inert atmosphere and then allowed to solidify therein. The solid so formed was then broken into large lumps. These lumps were then reacted with lumps of tetraethyl ammonium chloride and aluminium trichloride in varying quantities and under conditions shown in the Table 1 below to prepare six different batches (Batch Nos. 1-6) of acidic and basic melts. Lumps were used instead of powders to prevent charring of the melt during heating.

TABLE 1

Batch No.	[Et ₄ N]Cl (g)	[MeEtim]Cl (g)	AlCl ₃	Ternary Melt (g)	AlCl ₃ (Moles)
1	0.8922 (23.333%)	0.3936 (11.66%)	2.0	3.287	0.65
2	0.6958 (17.5%)	0.5922 (17.5%)	2.0	3.288	0.65
3	1.2428 (40%)	0.5498 (20%)	1.0	2.793	0.40
4	0.6214 (20%)	1.0996 (40%)	1.0	2.721	0.40
5	0.3107 (10%)	1.3745 (50%)	1.0	2.680	0.40
6	0.1553 (5%)	1.512 (55%)	1.0	2.667	0.40

[Et₄N]Cl is tetra-ethylammonium chloride

[MeEtim]Cl is 1-ethyl-3-methylimidazolium chloride

Ternary melt is [Et₄N]Cl/[MeEtim]Cl/AlCl₃

The ternary melts were characterised using ¹H NMR spectroscopy by placing the neat ionic liquid in a 4mm diameter NMR tube *in vacuo*.

- 5 No solvent was used for the analysis. The results of the analysis are tabulated in Tables 2 (standard melt) 3 and 4 (ternary melt) below:

TABLE 2

¹H NMR of Standard Binary C₁/C₂ Melt for Comparison

10

δ(ppm)	Intensity (I/I ₀)	Type
1.0	strong	triplet
3.4	very strong	triplet
3.8	medium	doublet
6.9	medium	doublet
7.8	medium	singlet

TABLE 3

¹H NMR of Ternary Melt (65% AlCl₃, 23.3% [Et₄N]Cl & 11.7% [MeEtim]Cl)

δ(ppm)	Intensity (I/I ₀)	Type
0.7	very strong	singlet
1.0	weak	singlet
2.6	very strong	singlet
3.3	medium	singlet
3.7	weak	doublet
4.6	very weak	singlet
6.8	very weak	doublet
7.8	very weak	singlet

[Et₄N]Cl - tetra ethyl ammonium chloride

- 15 [MeEtim]Cl - 1-ethyl-3-methyl imidazolium chloride

TABLE 4

¹H NMR of Ternary Melt (40% AlCl₃, 15% [Et₄N]Cl & 45% [MeEtim]Cl)

δ (ppm)	Intensity (I/I _o)	Type*
1.0	very strong	singlet
2.8	very weak	singlet
3.5	very strong	singlet
3.8	strong	singlet
7.4	medium	singlet
9.2	weak	singlet

* - all peaks were broad peaks

[Et₄N]Cl - tetraethyl ammonium chloride

5 [MeEtim]Cl - 1-ethyl-3-methyl-imidazolium chloride

EXAMPLE 2:

An ionic liquid was prepared in an inert atmosphere glove box consisting of three components, ie tetraethyl ammonium chloride (2.96g), 1-ethyl-3-methyl imidazolium chloride (9.17g) and aluminium trichloride (22.33g) in a mole ratio of 0.08 : 0.25 : 0.67 by the process described in our published EP-A-0558187. 5ml of the ternary melt ionic liquid so formed was dispersed into 200g of raffinate I feedstock (having an olefinic composition shown in Table 5 below) in 750 ml of heptane with stirring at atmospheric pressure and at 10°C for a duration of 180 minutes. The reaction was exothermic but a temperature rise of no greater than 10°C was observed during the reaction period. The yield of the polymer product was 68.5% wt/wt based on the weight of olefin present, ie 114.95 g of polymer product was obtained from 167.9g of olefin. The number average molecular weight of the polymer, Mn, was 1000.

TABLE 5

Raffinate I Feedstock Olefin	% wt/wt Concentration
Iso-butene	46.0
Butene-1	25.0
Trans-butene-2	8.2
Cis-butene-2	2.8
Saturated hydrocarbons	remainder

Comparative Test not according to the invention:

For comparison, an ionic liquid was prepared according to the process of Example 1 above but now consisting of 1-ethyl-3-methyl-imidazolium chloride (12.2g) and aluminium trichloride (22.3g). The components were present in the same mole ratio (A) : (b) of 2:1 and the polymerisation of raffinate I of the composition in Table 4 above was carried out in an identical fashion to that in Example 2 above. The yield of the polymer product in this case was 71.3g (42.5% w/w on olefin in the feed) and the number average molecular weight of the polymer, Mn, was 1000, ie the same as of the polymer in Example 2 above.

These results demonstrate that the use of a ternary melt ionic liquid as catalyst increases the rate of polymerisation of the monomer from 42.5% w/w of olefin fed (Comparative test) to 68.5% w/w of olefin (according to the invention).

Claims:

1. An ionic liquid comprising a ternary melt of
 - (a) a compound of the formula R_nMX_{3-n} wherein R is a C1-C6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1 or 2,
 - 5 (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide, and
 - (c) at least one of a hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide.
2. An ionic liquid according to Claim 1 wherein the compound (a)
10 is aluminium trichloride, gallium trichloride or ethyl aluminium dichloride.
3. An ionic liquid according to Claim 1 or 2 wherein the hydrocarbyl imidazolium halide is a 1,3-dialkyl imidazolium halide.
4. An ionic liquid according to Claim 3 wherein at least one of
15 the alkyl groups in the hydrocarbyl substituted imidazolium halide has more than 4 carbon atoms.
5. An ionic liquid according to any one of the preceding Claims 1-4 wherein the hydrocarbyl imidazolium halide is selected from the group consisting of: 1-methyl-3-ethyl imidazolium chloride, 1-ethyl-
20 3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium bromide, 1-methyl-3-propyl imidazolium chloride, 1-methyl-3-hexyl imidazolium chloride, 1-methyl-3-octyl imidazolium chloride, 1-methyl-3-decyl imidazolium chloride, 1-methyl-3-dodecyl imidazolium chloride, 1-methyl-3-hexadecyl
25 imidazolium chloride and 1-methyl-3-octadecyl imidazolium chloride.

6. An ionic liquid according to Claim 1 or 2 wherein the hydrocarbyl pyridinium halide is 1-alkyl pyridinium halide.
7. An ionic liquid according to Claim 1, 2 or 6 wherein the hydrocarbyl pyridinium halide is selected from the group consisting of:
5 of: ethyl pyridinium bromide, ethyl pyridinium chloride, ethylene pyridinium dibromide, ethylene pyridinium dichloride, butyl pyridinium chloride and benzyl pyridinium bromide.
8. An ionic liquid according to any one of the preceding Claims wherein the component (c) in the ternary melt is at least one of a
10 tetraalkyl ammonium halide and a tetraalkyl phosphonium halide
9. An ionic liquid according to Claim 8 wherein the component (c) in the ternary melt has 1-18 carbon atoms in each alkyl group.
10. A process for the conversion of olefinic hydrocarbons said process being selected from the group consisting of oligomerization,
15 alkylation and polymerization in the presence of an ionic liquid catalyst which has melting point below the process temperature, wherein the ionic liquid comprises (a) an aluminium halide or a gallium halide, (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted phosphonium halide
20 and (c) at least one of a hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide according to any one of the preceding Claims 1-9.
11. A process according to Claim 10 said process comprising polymerization of an olefinic hydrocarbon feedstock comprising one or
25 more of C2-C4 olefins.
12. A process according to Claim 11 wherein the relative mole ratios of components (a), (b) and (c) in the ionic liquid catalyst are such that (a) : [(b) + (c)] is in the range from 1 : 2 to 3 : 1 and (b) : (c) is in the range from 0.01:1 and wherein said catalyst
30 has a melting point below the process temperature.
13. A process according to any one of the preceding Claims 10-12 wherein the olefinic hydrocarbon feedstock for polymerization comprises ethylene, propylene, butene-1, butene-2 and/or isobutene.
14. A process according to any one of the preceding Claims 10-13
35 wherein the olefinic hydrocarbon feedstock is a raffinate from a

refinery process selected from raffinate I or raffinate II.

15. A process according to any one of the preceding Claims 11-14 wherein the polymerization reaction is carried out at a temperature from -50°C to +100°C.

5 16. A process according to any one of the preceding Claims 11-15 wherein the reaction is carried out either:

(i) by bubbling the olefinic hydrocarbon feedstock to be polymerized through the ionic liquid, or,

10 (ii) by dispersing the ionic liquid in appropriate concentration into the olefinic hydrocarbon feedstock to be polymerized and then subjecting such a dispersion to polymerization.

17. A process according to Claim 10 wherein olefinic hydrocarbon is used for alkylation of paraffins, isoparaffins or aromatics to form alkylates.

15 18. A process according to Claim 17 wherein the alkylation reaction is that of alkylating aromatics and is carried out at a temperature of eg below 100°C, suitably from -30 to +50°C.

19. A process according to Claim 21 wherein the mole ratio of the ionic liquid to the olefinic hydrocarbon used for alkylation is in the range from 1000 : 1 to 1 : 1000.

20 20. A process according to any one of the preceding Claims 17-19 wherein the aromatic hydrocarbon alkylated is benzene or toluene.

21. A process according to Claim 17 wherein during the alkylation of an iso-paraffin, the mole ratio of iso-paraffins to olefin is in the range from 1000 : 1 to 1 : 1000.

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INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/GB 95/00253

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F4/52 C07C2/54 C08F2/38 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 448 445 (INSTITUT FRANCAIS DU PETROLE) 25 September 1991 see claims 1-20	1-21
A	EP,A,0 558 187 (BP CHEMICALS LTD.) 1 September 1993 see claims 1-10	1, 10, 16
A	FR,A,2 611 700 (INSTITUT FRANCAIS DU PETROLE) 9 September 1988 cited in the application see page 2, line 18 - line 31; claims 1-10	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or the theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

26 June 1995

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. onal Application No

PCT/GB 95/00253

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0448445	25-09-91	FR-A- 2659871 JP-A- 4217633 US-A- 5104840	27-09-91 07-08-92 14-04-92
EP-A-0558187	01-09-93	JP-A- 5279422 US-A- 5304615	26-10-93 19-04-94
FR-A-2611700	09-09-88	NONE	